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RESEARCH ARTICLE

Producing Food Packaging Printing Ink via Green Emulsion Aggregation Method

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ABSTRACT

Digital printing will become more and more important in the packaging industry. Digital printing technology is growing because it allows the print suppliers to improve the level of service they offering to their customers, as well as, it opens new opportunities and helps them to make more money. Additives, dyestuffs, resin and other chemicals in packaging printing ink may influence safety of the food. Therefore, choosing suitable materials are very important in food packing ink. Over the last years, many printing ink manufacturers moved toward more sustainable inks. Drivers for this development, besides the resource scarcity and a higher legislative burden, are an increasing environmental awareness throughout the population and as a result a growing demand for inks with a small ecological footprint. In this regard, in this research due to the importance of electrophotographic printing in the printing industry, for the first-time we try to produce food packing ink for electrophotographic printing called toner by an eco-friendly EA method. The results show that, within the design of the toner, choosing suitable raw materials resulting in a toner with various color and appropriate toner properties.

KEY WORDS *Printing, Packaging, Food-grade dyes, Toner*

1.0 INTRODUCTION

In spite of the increasing importance of digital media over the last decades, printing still plays an important role in our daily lives and, for example, more than one million tons of ink is annually produced in Europe (EuPIA 2012). Even though the market for printed media is declining, there is an increasing demand for inks in other areas of the printing industry, such as packaging and digital printing. Therefore, the printing ink market is growing by 3% per year leading to an increasing in demand for traditional as well as new printing inks. In addition, resource scarcity, increased legislative burden, and rising environmental awareness force ink manufactures to develop more sustainable inks particularly for special applications such as packing (Robert 2015).

Printing inks are used to print on many different kinds of food packages (Leach 2007). During the last years, very intense studies were carried out to evaluate the potential of using digital printing techniques for packaging applications (Rosenberger and Boensch 2001). The reasons for doing this were so obvious and they still are due to achieve an economically affordable potential of making a short run for the test-sales. Having the opportunity of printing fully variable information can be used for producing more different consumer packaging or labels, in order to satisfy (and promote) the collector's mania of especially children (Deprez and Rosenberger 2003). Among all digital printing, the only technology that can deal with the desired printing speeds and image quality is electrophotography (Rosen and Ohta 2006). C.F. Carlson (Pell 1999) invented Electrophotographic printing in 1938 as a copying technology. This technology currently is in a high demand, and can be considered as the latest generation of publishing and printing industry (Marshall 1997). This method has attracted a lot of attention in the recent years as one of the major technologies for document printing and a wide range of market applications (Galliford 2008). Today, the total cost of ownership, convenience and quality, favor this technology over other alternatives in many applications (Ataeefard and Saeb 2015). Toner considered as the ink in digital electrophotographic printing, is polymeric particles compose of a polymeric resin as the main component, and various ingredients. The toner particles comprise at least one coloring substance such as black and/or other colored substances, such as colored pigments (Bazrafshan et al. 2015).

In order to apply electrophotographic techniques for food packaging, the ingredients of the toner need to satisfy the particular standards that are not generally required for other applications. For example, although various materials may be used to coat or mark pharmaceutical products, such materials would not necessarily be acceptable for food products (Pedersen et al. 2012). By "food-grade", in reference to a component, means that the component has been acceptable for use in foods (Innovateus). There are many aspects in food safety. The toxicology of the toner components plays an important role as well. However, with migration being a pivotal concern, dry toner does have an intrinsic advantage over other digital technologies. Migration depends on several factors, a major one is the size of the potential migrant molecule: The larger the molecule, the lower its mobility, and the less its tendency to migrate from one layer to another. The potential migrants differ depending on the digital print technology. In toner, the pigment particles are encapsulated in a high molecular weight polymer, therefore the migration decreases (Deprez 2012). Although, it is very important to choose appropriate component and integrant for food packaging ink. The European Printing Ink Association (EuPIA) (EUPIA 2011) regulates the use of printing inks for food packaging. Even only allowed materials can be used in the manufacture of food packaging inks such as additives, colorants, (pigments, dyes), pigment additives, polymeric resins, solvents or photo-initiators (Aznar et al. 2015).

In a previous work, author investigated the effect of mixing time, agitation speed, monomers ratio, carbon black content, surfactant concentration, magnetite and colorant on toner properties produced with various methods (Andami et al. 2016; Ataeefard 2015). Authors also produce toner with special applications such as antibacterial, fluorescence and ceramic toner (Ataeefard 2016; Ataeefard and Arabi 2014; Ataeefard and Nourmohammadian 2015). In the current work, we report an environmentally friendly fabrication method called emulsion aggregation (EA) for producing electrophotographic food-grade printing toner. The recently developed technique, known as emulsion aggregation (EA), was a chemically controlled process with the ability to yield toners exhibiting small particle size with narrow distribution and uniform shape. The importance of this method is indeed because of being environmentally friendly of both the process and resulting product.

In this regard, for the first time, 12 various kind of food-grade dyestuffs were used to prepare monodisperse semi-spherical composite with poly (styrene-co-acrylic acid) by using an eco-friendly EA method, which can be used as the food packing electrophotographic printing ink.

2.0 MATERIAL AND METHODS

2.1 Materials

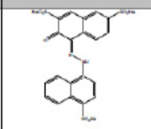
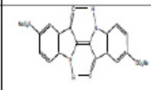
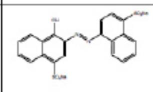
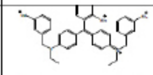
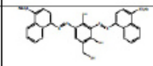
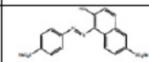
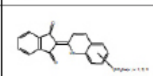
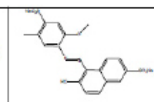
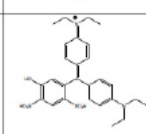
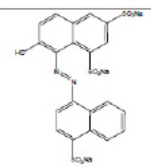
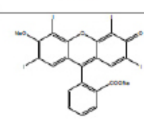
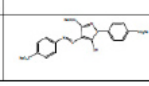
The polymer used in this study was a styrene-acrylic ;latex (R579; ResinFam Co., Iran) with a pH value of around 9, and Tg (glass transition temperature) of 51°C, and mean particle size of 220 nm, according to the specification provided by the supplier. A polyethylene emulsion wax was purchased from Kala Kar (EE 95, Kala Kar Co., Iran). Polyaluminum chloride from Merck Company was used as a coagulating agent. All the mentioned materials were used as received.

The characteristics of 12 food-grade dyes used for toner preparing in this study has been illustrated in Table 1.

2.2 Preparation of Packaging Printing Toner

Toner particles were produced via a stepwise procedure, in accordance with previous studies (Ataeefard and Saeb 2015; Bazrafshan et al. 2015). First (step *a*), a 1 L beaker was filled with 24.5 g styrene-acrylic latex, 2 g carbon black, 3 g wax, and 120 g deionized water and the contents were manually mixed at room temperature for about 15 min. In step *b*, the resulting suspension obtained in *a*, mixed using a homogenizer for 5 min. Next step, *c*, was started by continuous mixing of ingredients at room temperature for about 1 h followed by the addition of a solution of 0.6 g coagulation agent in nitric acid over 10 min until reaching the pH value of the mixture to 2. In this manner, forming a gel was observed, as a result of a change in the visco-elastic nature of the suspension from a Newtonian

Table 1: Characteristics and structures of food grade dyes used for packaging toner preparing

Dye	C.I. Number	E Number	Commercial Name	Structure	Formula	Observed Color
1	16185	E123	Amaranth		$C_{20}H_{11}N_2Na_3O_{10}S_3$	Dark Red To Purple
2	73015	E132	Indigo Carmine		$C_{16}H_8N_2Na_2O_8S_2$	Blue
3	14720	E122	Carmoisine		C20H12N2 Na2O7S2	Red To Maroon
4	42090	E133	Brilliant Blue FCF		$C_{37}H_{34}N_2Na_2O_9S_3$	Reddish-blue
5	20285	E155	Chocolate Brown HT		$C_{27}H_{18}N_4Na_2O_9S_2$	Brown
6	15985	E-110	Sunset Yellow FCF		C16H10N2 Na2O7S2	Orange
7	47005	E104	Quinoline Yellow WS		$C_{18}H_{13}NO_{5/8/11}S_{1/2/3}Na_{1/}$	Greenish Yellow
8	16035	E129	Allura Red AC		$C_{18}H_{14}N_2Na_2O_8S_2$	Red
9	42051	E 131	Patent Blue V			Blue
10	16255	E124	Ponceau4R		$C_{20}H_{11}N_2Na_3O_{10}S_3$	Strawberry Red
11	45430	E127	Erythrosine		C20H6I4Na 2O5	Cherry-Pink
12	19140	E-102	Tartrazine		$C_{16}H_9N_4Na_3O_9S_2$	Yellow

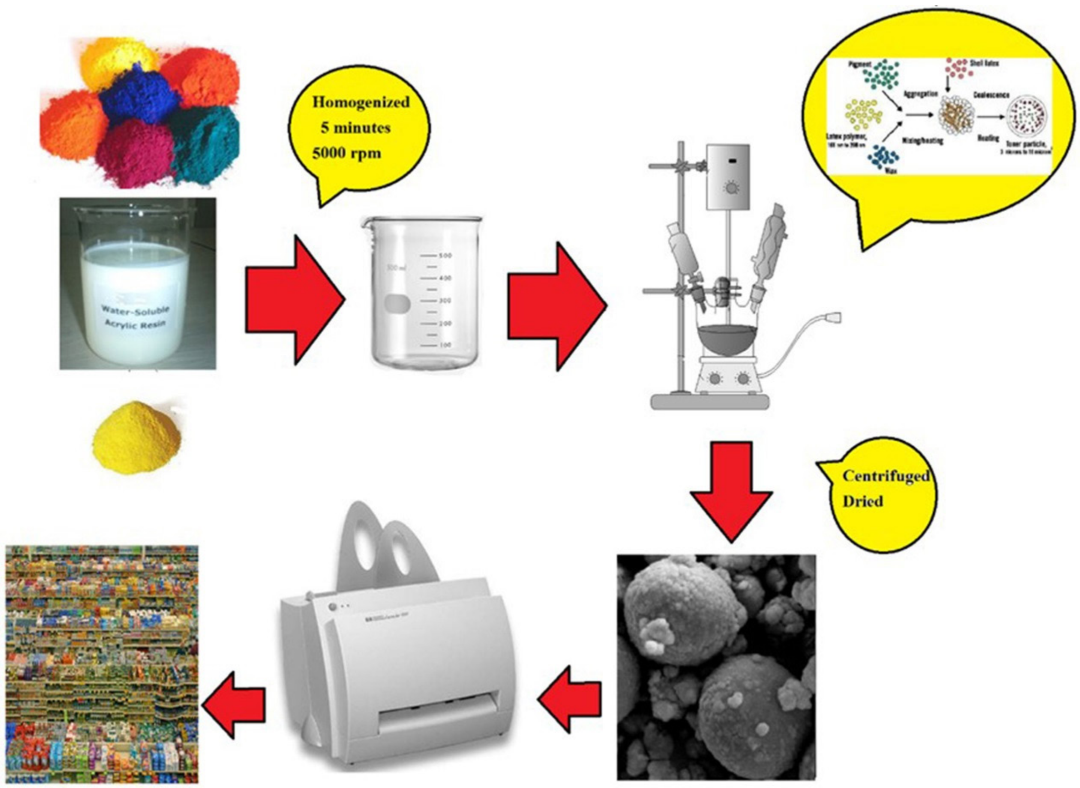


Figure 1: Schematic of toner preparing method

water-like fluid to a shear-thinning paste-like gel. In step *d*, the temperature of the mixture rose to 50°C for about 30 min while the gel was continuously mixed. The mixture was held at this temperature for another 60 min in step *e*, where the temperature of the mixture increased to 96°C for 30 min. The last step, denoted as *g*, was started by holding the product of step *f*, at 96°C for a further 60 min. Fig 1 shows the schematic of toner preparing method.

The ultimate mixture was neutralized with sodium hydroxide solution and cooled down to 25°C, then the produced microparticles were isolated from the water, washed to remove divalent ions, filtered, and dried using a frizzed dryer. Table 2 shows food-grade dyes and produced packaging toners.

The obtained toner were printed in a controlled environment [23°C, 50% relative humidity (RH)]

Table 2: Image of food-grade dyes and produced toners

Dye	Image	Toner	Image	Dye	Image	Toner	Image
1		1		7		7	
2		2		8		8	
3		3		9		9	
4		4		10		10	
5		5		11		11	
6		6		12		12	

using a monochrome laser-jet printer (HP 1100, Laser-jet printer). This printer was changed; in order to only have hot roll fusing system containing two metal rolls covered with silicone rubber and was heated from inside the rolls.

2.3 Characterization of food grade dyes and food grade printing toner

The reflectance measurement of the dye and toner was performed in the range of 380 -780 nm with 10 nm intervals using a GretagMacbeth Color Eye 7000A spectrophotometer (USA), an instrument with 8/d geometry in a specular component including (SCI) mode. Then it transformed into CIE LAB colorimetric coordinates (*L*, a*, b**) by using CIE standard illuminant D65 and a CIE 1964 standard colorimetric observer. All measurements were carried out on five different positions of each sample, and the average value was reported. An increase in *L** indicates the lightening of a sample. A positive Δa^* signified a color shift toward red; a negative Δa^* signifies a color shift toward green. Similarly, a positive Δb^* signifies a color shift toward yellow; and a negative Δb^* indicates a color shift toward blue (Fairchild 2005).

The obtained color toners were centrifuged and dispersed in water followed by a sonication for about two minutes in order to break aggregations. The dispersions were prepared for analyses of particle size and the measurements of particle size distribution by using particle size analyzer (PSA, Malvern Rasterizer 2000, England) in the range of 0.02-2000µm. The evaluation of the particle size distribution (PSD) was normally achieved through the span parameter, as follows:

Where D50 denotes the diameter (µm) at which half of the particles have a size below this value. Similarly, D90 and 10 were defined.

Morphology of the pigmented composite toners was studied by scanning electron microscopy (SEM, KYKY-EM3200, China).

Thermal behavior of the toner was conducted on a differential scanning calorimeter (DSC, PerkinElmer USA). Approximately 5 mg of each sample was loaded onto a pan and sealed with a covering lid. The measurements were performed over a

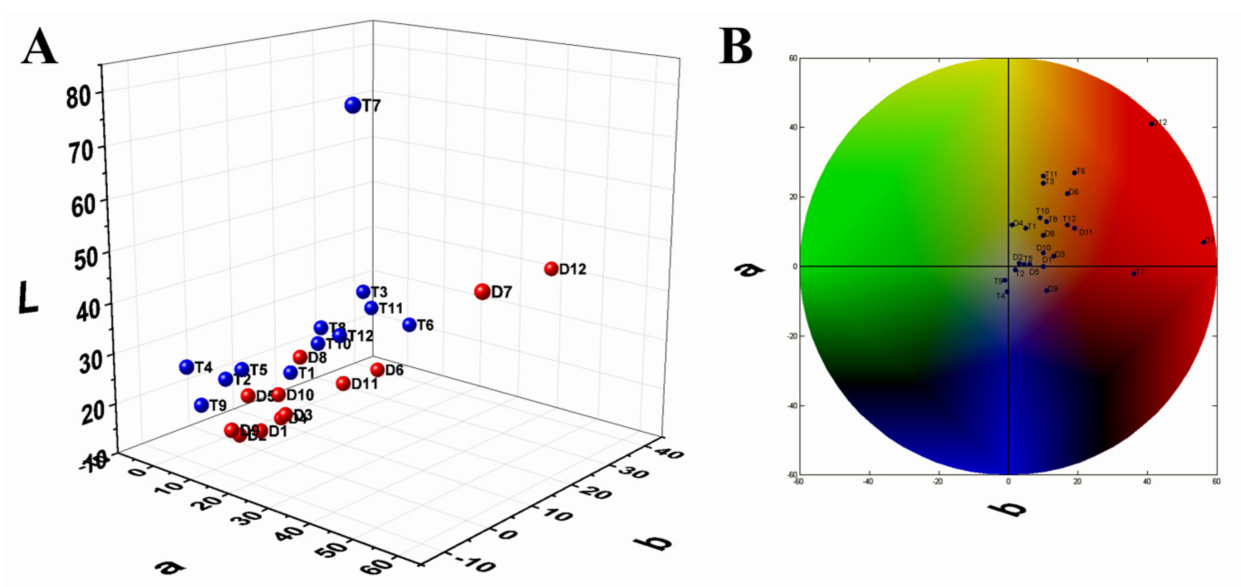


Figure 2: (A) the colorimetric coordinates (L, a*, b*) of the food grade dyes (D1 to D12) and toners (T1 to T12) and (B) 2D projection of them*

temperature range of 0-150 °C at a heating rate of 10 °C/min in an atmosphere of nitrogen.

3.0 RESULT AND DISCUSSION

Fig 2A shows the colorimetric coordinates (*L*, a*, b**) of the food-grade dye (**D1** to **D12**) and packaging toner (**T1** to **T12**) and 2D projection of it (Fig 2B).

Although, we tried to choose color in the various range of color contain blue and brown. The results showed that the most of food packing toner colors located in the yellow and red region of the CIE LAB color space due to its large positive amount of b and a. Colors often have different meanings in various cultures. And even in Western societies, the meanings of various colors have changed over the years .While blue is one of the most popular colors it is one of the least appetizing. Blue food is rare in nature. Food researchers say that when humans searched for food, they learned to avoid toxic or spoiled objects, which were often blue, black, or purple. When food dyed blue is served to study subjects, they lose appetite. Green, brown, and red are the most popular food colors (Johnson 2007).

The color difference results between toners and dyes showed that introducing the dye into the resin to produce toner would change the color characteristics. Fig 3 results show that almost all samples have shown an increase in lightness

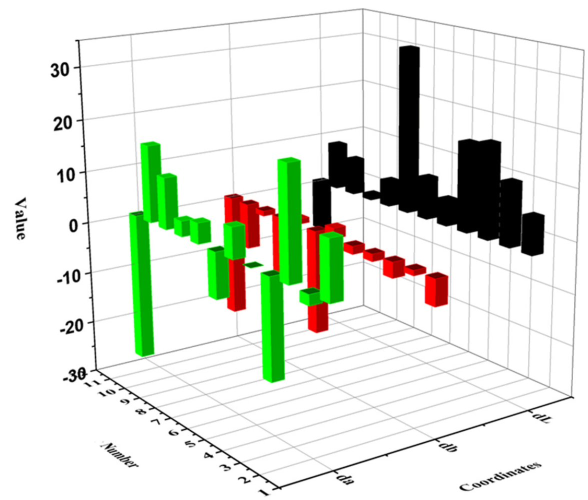


Figure 3: The color difference between food grade dyes (D1 to D12) and toners (T1 to T12)

(*L**) due to using white acrylic resin with a high amount of lightness.

In general, the physical properties of the toner particles including shape, particle size and particle size distribution play a vital role in determining the quality of digital printing created by photocopiers and laser printers (Kmiecik-Lawrynowicz 2003). Fig 4 shows the SEM micrographs of the three selected packaging toner particles (**T9** as cyan toner, **T11** as magenta toner and **T7** as yellow toner). It can be seen that the toner particles formed from a completely spherical shape to an almost spherical shape or potato shape. Moreover, SEM images of

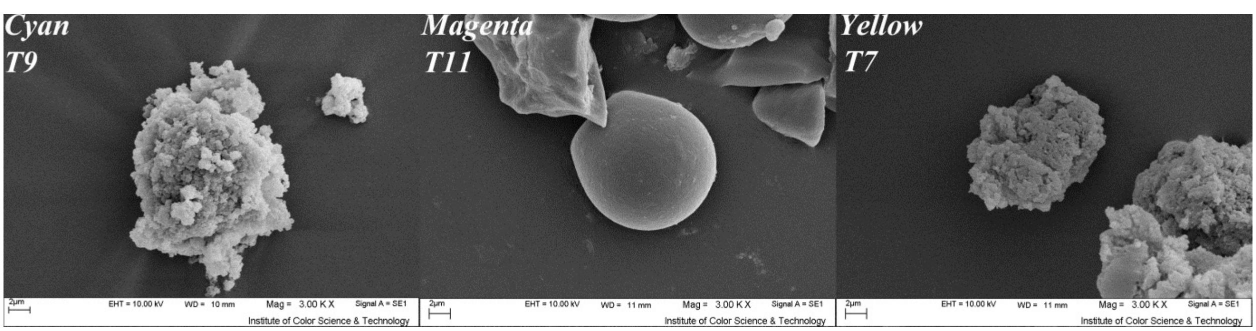


Figure 4: SEM image of three selected packaging toner particles (T9 as cyan toner, T11 as magenta toner and T7 as yellow toner)

toners show that the particles have a rough surface. This phenomenon can be attributed to the particular surface tensions of the toner's constituents that have resulted from the migration of the dyes from the inner part of the particle to the surface (Bazrafshan et al. 2014). Therefore, as the compatibility of a polar dye with the toner medium is high, the dyes migration to the surface and the toner surface roughness have reduced.

With Regard to the difference in the obtained SEM micrographs and toner particle shapes and roughness (Fig), **D11**, is more polar than two others dyes, and revealed a better compatibility with the toner medium. Consequently, toner with desired spherical particles could be obtained. A comparison between toner with **T7** and **T9** dye showed that **D7** is more compatible with the toner medium and caused to produce a toner with more spherical shape than **D9**. In the previous study (Bazrafshan et al. 2014; Bazrafshan et al. 2015), the authors showed that the physicochemical properties (polarity and compatibility) of pigments do not affect the toner shape, while the physicochemical properties of dyes significantly affect the toner shape.

The thermal characteristics of the packaging toners, namely T*g* (glass transition temperature), are important. This importance is due to having a direct effect on the fixing properties of toners onto the paper substrate. A moderate T*g* value is generally required for the toner to have appropriate fixing properties. A too high Tg would result in a large-scale energy consumption during the printing process, and a too low T*g* causes the toner to stick to the printer cartridge. For an industrial toner, to have suitable fixing properties for an energy-efficient laser printing, T*g* should normally be in the range of 50 to 70°C (Einarsson 2002). The results of DSC analysis show a packaging toner between 60-80°C. The results show that the T*g* (endothermic event in the DSC diagram) is in an appropriate range. Therefore, changing the dyes did not affect the thermal properties of toner.

Fig 5 shows the decomposition (TGA and DTG) diagram of packaging and original toner. All toner has followed one main decomposition step at around 400 °C confirmed by derivative thermogravimetric (DTG). Packaging and original toner also show almost different decomposition rate, and starting decomposing temperature (T*onset*). Among all toners, the fastest rate of decomposition and the lowest T*onset* belong to the produced toner with **D7** dyes, and the slowest rate of decomposition and the highest T*onset* belong to the original toner.

After the thermal decomposition of organic

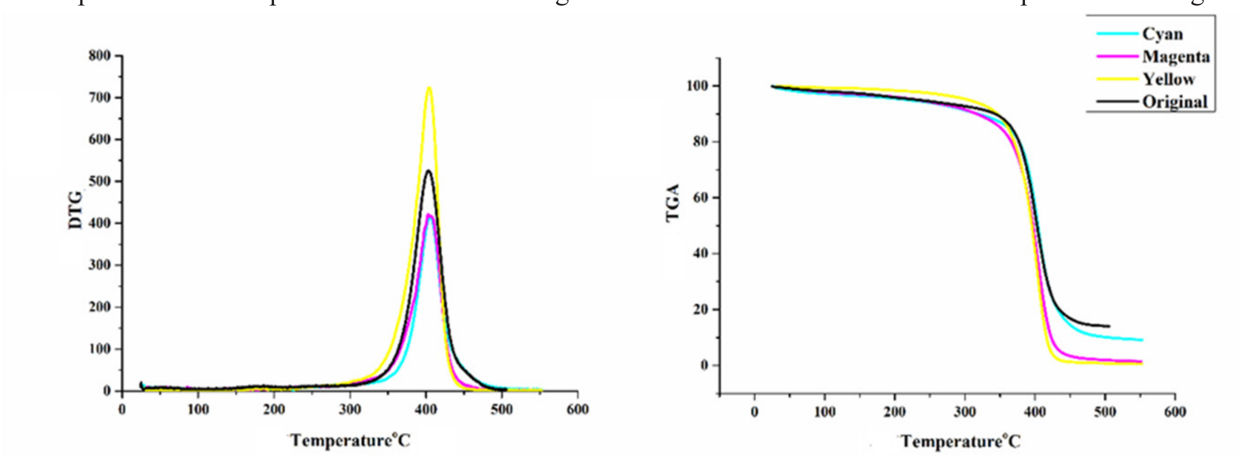


Figure 5: TGA and DTG image of three selected packaging toner particles (T9 as cyan toner, T11 as magenta toner and T7 as yellow toner) and original toner

constituents at high temperatures, the residual weight percentage of the sample can be considered as the inorganic content (Ataeefard and Sharifi 2014), which is different from packaging toner and original toner. Among all toners, the lowest char belongs to the produced toner with **D7** dyes, and the highest char belongs to the original toner.

4.0 CONCLUSION

The aim of this work was to produce packaging electrophotographic printing ink (toner), and to investigate the effect of colorant type on the physical and fluorescence properties of toner. Therefore, 12 food dyes were used to prepare monodisperse semi-spherical composite with poly (styrene-co-acrylic acid) by using an eco-friendly method named emulsion aggregation (EA). The results show that through determination of thermal and microscopic features of the toners, where both the size and glass transition temperature situated in the satisfactory interval proposed for industrial toners. Results demonstrate that **11D** dye had higher polarity, better compatibility and dispersion, and produced toners with more circular shape.

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